Final Report for "Strategic Partnership for Research in Nanotechnology" September 2005 to February 2008

Project Number: FA9550-05-1-0478
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Center for Nano and Molecular Science and Technology

This final report details recent work at The University of Texas at Austin that has been enabled through the Strategic Partnership in Nanotechnology (SPRING) grant and the shared research equipment it has provided. Highlights of accomplished research are presented below have either received support directly from awarded funds or used shared research instrumentation purchased with monies from this grant. Equipment purchased with these funds is located in the Nano Science and Technology building inside of which the Center for Nano and Molecular Science and Technology (CNM) is located. In total over 400 faculty members, students, and staff from UT Austin have access to SPRING support. During the SPRING timeframe, more than 300 peer-reviewed reports have been published that are a direct result of UT-Austin SPRING funding.

Funding provided to the University of Texas through the SPRING grant has enabled a tremendous amount of world-class research to be carried out, additionally it has also been used to augment nano-related programs at the University. Faculty hiring, retention, graduate student recruiting, scholastic outreach, and inter- and intra-University collaboration have all substantially benefited from the growing locus of nano-research and activities sponsored in part by SPRING.

Much of the research enabled by the SPRING program can be assigned to two categories: "Nanotechnology for Energy Needs" and "Nanoelectronics". With the broad audience our instruments are available to, there is a diverse set of topics on which research is performed including: nano-bio materials, nanoparticle synthesis, drug delivery, and micro-fluidics.

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1. Nanotechnology for Energy Needs

The CNM faculty members are tackling new problems in two major areas of renewable energy: photovoltaics and hydrogen fuel cells. The CNM efforts couple basic science with engineering to develop new materials, understanding, and devices.

Paul Barbara (Chemistry and Biochemistry) and his research group have developed fundamental research on photovoltaics including work on electrochemical studies of organics, single molecule spectroscopy of organic materials in device architectures, and nanoparticle synthetic research. They have recently demonstrated a novel and powerful method to study electrogenerated chemiluminescence (ECL) of single nanoparticles of conjugated polymers on electrodes.[1] Along with Allen Bard and his research group Barbara has developed a single-molecule spectroelectrochemistry (SMS-EC) method to unravel complex electrochemical process in heterogeneous media. This technique has been used to study the oxidation of nanoparticles of the conjugated polymers. Agreement between experimental data and simulations strongly supports the presence of deep traps in the studied nanoparticles and highlights the ability of SMS-EC to study energetics and dynamics of deep traps in organic materials at the nanoscale.[2] Other recent research has focused on how the spectroscopic properties of conjugated polymers evolve in the size range between single polymer chains and bulk material. [3] This work shows that MEH-PPV nanoparticles greater than 10 nm in size have spectroscopic properties of the bulk material.

Also working in the area of photovoltaic research is **David Vanden Bout's** (Chemistry and Biochemistry) group. They utilize high-resolution optical microscopy techniques that are capable of mapping out fluorescence lifetimes on the nanoscale to probe charge separation in conjugated polymer thin films. [4-7] Initial charge separation is critical to the success of any photovoltaic device. The group has fabricated a silicon microprobe integrated with a nanometer-sized light emitting diode (Nano-LED) on the tip.[8]

Brian Korgel's (Chemical Engineering) and coworkers have developed a vast array of synthetic strategies for the controlled production of nanostructures comprised from many materials including recent work on: ultrathin gold nanorods,[9-11]silicon nanowires,[12-14], CdTe/CdSe/CdTe hetero rods,[15] magnetic FePt and MnPt

nanoparticles, [16, 17] mechanistic and structural nanowire observations, [18-21] oriented columns of nanodisks, [22] using nanoparticles in cancer cell imaging strategies including two-photon tumor imaging accomplished by directed nanoparticle targeting. [23-25]

Keith Stevenson's (Chemistry and Biochemistry) group has recently reported on the synthesis of 3 nm magnetic NiAu nanoparticles using PAMAM dendrimers as nanoparticle templates.[26] They have also used the dendrimer-templated growth approach to assemble platinum catalysts onto carbon nanotubes.[27] Their group is also working on characterization of charge transport behavior in organic and metal oxide thin films. This project focuses on the development of high resolution optical and scanning probe microscopy tools for evaluation of charge transport in heterogeneous, nanostructured materials. Spatially resolved measurements obtained at nanoscopic length scales aids in the understanding of structure-property and materials performance relationships crucial for the development of next-generation batteries, fuel cells, and solar cells. Recently their group has been able to assemble Pt nanoparticles onto nitrogen – doped carbon nanotubes for oxygen reduction. [28]

Allen Bard's (Chemistry and Biochemistry) research group has continued to work on screening arrays of new mixed metal nanoparticle electrocatlysts for oxygen reduction, a key step in proton exchange membrane fuel cells. They have developed a technique that utilizes scanning electrochemical microscopy to rapidly study novel materials fabricated by a combinatorial synthesis strategy. These efforts continue to lead to the discovery of several new electrocatlysts. [29-32]

Nanoscale catalysts have shown promising properties for a number of critical applications related to renewable energy and green chemical synthesis, because of their high surface to volume ratio and the ability to produce nanoparticles of a wide variety of sizes and shape. The laboratory of **Richard Crooks** (Chemistry and Biochemistry) has developed a new method for the synthesis of monodisperse dendrimer-encapsulated metal nanoparticles with well-defined stoichiometry and are currently studying: the large degree of disorder in metal nanoparticles,[33] mixed Pd-Pt catalyst particles,[34] dynamics in core-shell particles.[35] **Paulo Ferreira** has recently found that the amount

of plastic strain caused by the motion of a single dislocation across an individual nanosize grain is drastically higher than the amount recorded for larger grain sizes. As a result, in nanocrystalline materials, only a small number of dislocations need to move within individual grains to accommodate plastic strain.[36] They have also investigated the formation mechanism involved with individual Pt nanoparticles as catalysts in membrane fuel cell. [37]

2. Nanoelectronics

A key emerging area in nanotechnology is nanoelectronics. The CNM works with the Microelectronics Research Center (MRC) at the University of Texas' Pickle Research Campus to jointly push forward the development of nanoscale electronics. These efforts include both fundamental research on materials as well as applied engineering and testing of new nanoscale devices.

Anath Dodabalapur (Electrical and Computer Engineering) is a world-leaded in the field of organic electronics. Recently his group has produced high-mobility organic thin film transistors on a variety of different organic materials and organinc/inorganic hybrids.[38-40] His group has performed measurements on both the drift mobility[41, 42] and charging phenomena[43, 44]of organic thin-film transistors as well as demonstrated applications involving bio-sensing,[34, 45, 46] photovoltaics,[47] and as active elements in micro-fluidics.[48, 49]

Li Shi (Mechanical Engineering) is creating nanowires of thermoelectric materials. Based on theoretical calculations these nearly one-dimensional structures should have exceptional thermoelectric properties. After synthesis of a batch of nanowires, individual nanostructures are placed onto a micron-sized thermal test bed structure that was developed and fabricated in Shi's laboratory.[50-53] A second important project in the Shi group is the high-throughput nanofabrication strategy to produce highly monodisperse, enzymatically-triggered nanoparticles of precise sizes and shapes for drug delivery.[54]

One area of Nanoelectronics research is "quantum engineering" of metallic and magnetic structures. **Ken Shih** (Physics) investigates how quantum confinement of electronic states impacts the thermodynamic properties of metallic nanostructures and

how such confinement influences the collective bulk electronic properties such as magnetism and superconductivity. [42, 55]

Sanjay Banerjee's group has for the first time demonstrated that a chaperonin protein lattice can be used as a template to assemble nanocrystal (NC) arrays for Flash memory fabrication. [56] Their methodology provides a new approach that can incorporate different types of NCs from a colloidal suspension for Flash memory fabrication. [57] The group is also modeling the transport behavior in individual nanowire transistors. [58-60]

Shaochen Chen (Mechanical Engineering) has developed a method to directly pattern 3-D nanostructures by plasmon-assisted nanolithography. [61] Their group is also modeling nanostructured emitters based on a combination of cavity enhancement with a surface plasmon. [62]

The CNM efforts in nanoelectronics efforts are also branching out from traditional semiconductors and into emerging areas such as spintronics. **Maxim Tsoi's** (Physics) research is focused on this new technological discipline that refers to studying the role played by an electron spin in solid-state physics.[63, 64] The main focus of his work is in current driven spin-transfer phenomena. [65] His research group has recently demonstrated transfer of spin-angular momentum across and interface between ferromagnetic and anti-ferromagnetic metals. The spin transfer is mediated by an electrical current and revealed by variation in the exchange bias at the ferromagnet/antiferromagnet interface. Current-mediated variation of exchange bias can be used to control the magnetic state of spin-valve devices, e.g., in magnetic memory applications which create an entirely new class of high-density non volatile memory. [66]

3. Shared Research Instrumentation Purchases

The SPRING at UT-Austin research program has allowed researchers the ability to add infrastructure and new instrumentation to the CNM facilities. These facilities are available to researchers from UT-Austin, other outside Universities, and corporate customers. Shared research facilities located in the CNM are managed in a way that provides facile electronic: training, reservation, physical access, and invoicing. Our instrumentation is used by over 300 undergraduates, graduates, and post-doctoral fellow

from UT-Austin and beyond. Also there are five corporate partners making use or our shared instrumentation.

The major purchase with these funds is an organic device fabrication and photo-characterization system housed in an oxygen and water free glove-box system. The fabrication system incorporates spin-coating, thermal vapor deposition, e-beam sputtering, and RF plasma sputtering with shadow mask lithography inside an anhydrous and anaerobic environment. The photo-characterization system measures both solar-simulated conversion efficiency and spectroscopic quantum efficiency. Both systems are built to operate in a turn-key fashion. This facility is being used to construct thin-film photovoltaic devices. These devices are based on either organic or semiconductor heterojunctions.

An inductively coupled plasma-enhanced chemical vapor deposition (ICP-PE-CVD) tool was purchased for the low-temperature deposition of: silicon oxide, amorphous silicon, silicon nitride (low stress and stoichiometric) and silicon oxynitride. The ICP-PE-CVD is also setup to perform Bosch and cryogenic process deep reactive ion etching of silicon. The ability to grow a number of low-temperature materials with selective high-aspect ratio etching makes this a key tool in our MEMS/NEMS fabrication abilities.

Other equipment purchased with these funds includes: microscope for single molecule spectroscopy, inkjet materials printer (direct-write nanoparticle patterning), vacuum chamber (housing a controlled atmosphere single molecule spectroscopic microscope), high-sensitivity CCD camera (single molecule spectroscopy).

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